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(19)

(54) SHAPED CATALYST PARTICLES AND HYDROTREATING PROCESSES EMPLOYING THE SAME

(71) We, AMERICAN CYANAMID COMPANY, a corporation organized and existing under the laws of the State of Maine, United States of America, and having its executive offices at Wayne, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to shaped, porous catalyst particles useful in hydrotreating petroleum residuum, and to a petroleum residuum hydrotreating process employing the catalyst particles.

In the past, catalyst materials used in hydrotreating processes were generally of spherical or cylindrical shape. Such convex catalyst particles provided desirable activity for the specific hydrotreating processes considered at the time. Since the particles also had desirable physical properties and were readily prepared, little interest was devoted to novel catalyst shapes and sizes. The lack of interest apparently arose because it was felt that small particles would cause intolerable pressure drops, that distinctive shape would have adverse effect on physical properties, that no advantage would arise from shape distinctions, and, in fact, that any increased void fraction would reduce reactor activity because of the lesser weight of catalyst present per reactor volume occasioned by the larger void fraction.

Recent shortages in petroleum supplies coupled with increased demand for products thereof have necessitated reliance on secondary sources in increasing amounts. These secondary sources require more extensive hydrotreating and are more difficult to process. Use of conventional spherical or cylindrical catalyst particles does not result in efficient hydrotreating of petroleum residuum. Recourse must be had to more effective catalysts for hydrotreating if the shortages are to be alleviated by resort to secondary sources.

In United States Patent 3,674,680 to Hockstra et al., there is disclosed a process for hydrotreating petroleum residuum by use of small catalyst particles of distinct shape, which at the same time, have a majority of pores having a diameter in the range of 100—200 Angstrom units. The catalyst is said to provide an increased service life over conventional catalysts and the extended life is thought to be due to the combination of the large-pore alumina substrate and small particle size, with the shape characteristics providing reduced pressure drop compared to normal shaped small particles. Although this U.S. Patent provides a catalyst of extended service life, it does not provide improved activity in use. Since activity decreases with service life, the extended service life provided is at a low level of activity.

There continues to exist, therefore, the need for hydrotreating catalysts useful in processing petroleum residuum that not only provide extended service life but also provide improved activity throughout service life of the catalyst particles.

In accordance with the present invention, there is provided a porous, hydrotreating catalyst particle having a composition comprising a major portion by weight of alumina, optionally up to 36 weight percent of silica, based on the total weight of silica and alumina; from 10 to 20 weight percent of molybdenum oxide, and a total of 1 to 8 weight percent of an oxide selected from cobalt and nickel oxides and mixtures thereof, said percentages being based on the total weight of said catalyst particle; said particle being in the form of a concave geometric solid; said solid being characterized by a concavity index greater than 1.0, a void fraction in the range of 0.25 to 0.60, a particle size defined by a ratio of geometric volume to geometric surface in the range of 0.001 to 0.042 inch, a catalytic surface area greater than 150 square meters per gram, and a catalytic pore volume in the range of 0.35 to 0.85 cubic centimeters per gram; said pore volume resulting from a major portion of pores of diameter in the range of 40 to 90 Angstrom units when measured with mercury at up to 50,000 pounds per square inch absolute pressure and a contact angle of 140°.

In accordance with the process aspect of the present invention, there is provided a process for hydrotreating a petroleum residuum, which process comprises contacting said residuum with a fixed bed of catalyst particles of this invention in the presence of hydrogen at a flow rate of 500 to 5,000 standard cubic feet per barrel of residuum, at a liquid hourly space velocity of 0.20 to 5.0 reciprocal hour, at a temperature in the range of 600 to 850° F., and at a total pressure in the range of 200 to 10,000 pounds per square inch gauge.

Unexpectedly, the present invention in preferred instances provides catalyst particles that are improved in activity and show lower decreases in activity with time of service than do prior art catalysts.

In order that the size and shape characteristics of the catalyst particles may be clearly understood, the following discussion is given.

Concavity Index.

A geometric solid is convex if all pairs of points lying within or on the cross-sectional surface of the solid can be connected by a straight line which is completely contained within or on the surface thereof. Conversely, a geometric solid is concave if pairs of points lying within or on the cross-sectional surface of the solid can be connected with a straight line which is not completely contained within or on the surface of the solid. The geometric volume of a convex solid of the minimum size necessary to contain a concave solid will be greater than the geometric volume of the concave solid. Letting V_x equal the volume of the minimum convex solid and V_o equal the volume of the contained concave solid, the Concavity Index, C, is given by the expression:

$$C=V_x/V_o$$

In order for the geometric solid to be concave, the value of Concavity Index must be greater than 1.0. Since the present invention requires concave solids, the Concavity Index must be greater than 1.0 and preferably is 1.05 to 1.15.

Void Fraction.

The void fraction represents the closeness of particle packing that can be obtained with particles of a given shape. In a given geometric volume of space, a specific number of catalyst particles can be packed. Multiplying the geometric volume by the number of particles, a total geometric particle volume, V_p, is obtained. If the apparent geometric volume of space packed is V_s, there will exist void space V_v, not actually occupied by catalyst particles. Thus, $V_s=V_p+V_v$. The void fraction, E, associated with a given shape is given by the expression

$$E=\frac{V_v}{V_s}=\frac{V_v}{V_v+V_p}.$$

In order for a catalyst particle to be useful, in accordance with the present invention, it must have a void fraction in the range of 0.25 to 0.60, preferably from 0.35 to 0.50.

Ratio of Geometric Volume to Geometric Surface.

Catalyst particles of the present invention have a characteristic volume and geometric surface area associated therewith as a consequence of their cross-sectional shape and length. The geometric volume and geometric surface area are readily calculated from appropriate measurements associated with the perfect geometric forms. Actual catalysts approximate such forms and their volumes and surface areas can be closely estimated from the corresponding geometric models. The ratio of geometric volume to geometric surface area is indicative of particle size and should be in the range of 0.001 to 0.042 inch, preferably from 0.005 to 0.025 inch.

In addition to the geometric considerations reflecting particle size and shape, it is also necessary for the catalyst particles to possess certain characteristics that are associated with catalytic action. These characteristics and methods of measurement are given next.

Catalytic Surface Area.

The catalytic surface area is expressed in square meters per gram and is determined in accordance with the procedure described by H. W. Daescher and F. H. Stross in Anal. Chem., Vol. 34, page 1150, 1962. This value should be greater than 150 square meters per gram, preferably greater than 200 square meters per gram, and more preferably from 250 to 300 square meters per gram.

Catalytic Pore Volume.

The catalytic pore volume of the catalyst particles represents internal cavities therein. Measurements are made by conventional procedures based on mercury penetration at 50,000 pounds per square inch absolute pressure using the contact angle of 140°. In this procedure, both total pore volume and pore diameter are determined. Catalyst particles of the present invention will have a total pore volume in the range of 0.35 to 0.85 cubic centimeters per gram with the majority of the pores having a diameter in the range of 40 to 90 Angstrom units in accordance with the method of determination specified.

A preferred shape for the catalyst particles of this invention is a "three-leaf clover" shape such as shown in Fig. 8 of the accompanying drawings. More precisely, this shape is identified as a trilobal cross-sectional shape such that the lobes are defined by

circles having centers and equal diameters, the centers of which circles are spaced from each other so that lines joining their centers form an equilateral triangle.

In addition to the geometric size and shape relationships and the catalytic characteristics, the catalyst particles will also have a specific chemical composition, which is next discussed.

The catalyst particles will comprise a major portion by weight of alumina and, in particular, small-pore alumina so as to be consistent with the catalytic characteristics specified above. The alumina will thus be the major structure-forming component of the catalyst particles. In addition to alumina, the catalyst particles may contain up to 36 weight percent of silica, based on the total weight of silica and alumina. The amount of silica added as such will generally be up to 5 weight percent, same basis. When added in the form of aluminosilicate, such as a zeolite, it may be as high as about 45 weight percent of zeolite, thus giving rise to 36 weight percent maximum of silica, as indicated.

The catalyst particles will also contain from 10 to 20 weight percent of molybdenum oxide and from 1 to 8 weight percent of an oxide selected from cobalt and nickel oxides and mixtures thereof. These constituents serve as promoter materials and are based on the total weight of the catalyst particle.

In the preferred method for preparing the catalyst particles of the present invention, precipitated alumina is prepared in accordance with conventional procedures, well-known in the art. After filtration, washing, and adjustment in composition as may be desired, the precipitated alumina is spray-dried in accordance with conventional procedures. The spray-dried alumina powder may then be prepared as an extrusion mix, incorporating therein, if desired, the promoter ingredients. Typically, mix-mulling is employed in providing the extrusion mix. The extrusion mix is then extruded through a die having orifices of the desired cross-sectional shape and the extrudate is cut to the proper length to provide the desired shape characteristics specified. The extrudate is then subjected to drying and calcination in conformity with conventional procedures. If provision for promoter incorporation was not made prior to extrusion, the calcined extrudate may be suitably treated with promoter materials and again calcined, in accordance with conventional procedures. Advantageously, preparation of catalyst particles of the present invention requires no new processing steps, but merely requires conventional processing directed to the novel combination of geometric, catalytic and compositional features of the catalyst particles as described.

In addition to extrusion, catalyst particles of the present invention may be prepared by other procedures. For example, the shaped articles can be obtained by tabletizing or pelletizing, or molding, etc.

The catalyst particles prepared as described are useful in hydrotreating petroleum residuums. In hydrotreating reactions, three effects are observed. Primarily, hydrodesulfurization is accomplished. Hydrocracking, to a limited extent, and nitrogen removal may also occur. Accordingly, hydrotreating is the preferred term used to describe the catalytic reactions effected since it is generic as to the effects observed.

In carrying out the process of the present invention, a petroleum residuum is contacted with the catalyst particles described in the presence of hydrogen gas at specified values of temperature, pressure, and space velocity. The catalyst particles are present in the form of a fixed bed and generally several beds are employed. Preferably, the catalyst particles are first subjected to a preliminary sulfiding but even if this step is omitted the catalyst will eventually be in the sulfide form because of the hydrogen sulfide evolved in the hydrotreating. In carrying out the hydrotreating, the hydrogen gas and residuum are mixed and fed downward through the catalyst bed. Catalyst bed size and residuum flow rate are adjusted so as to provide a liquid hourly space velocity in the range of 0.20 to 5.0, preferably 0.2—0.8 reciprocal hour. Hydrogen flow rate is from 500 to 5000 standard cubic feet per barrel of residuum, preferably 2000—4000. The reaction temperature is in the range of 600° to 850° F. preferably 650°—750° F. and the total pressure is from 200 to 10,000, preferably 600 to 1,000 pounds per square inch gauge.

By using the catalyst particles of the present invention in the hydrotreatment of petroleum residuum according to the process described, good hydrodesulfurization activity is obtained. In addition, the catalyst particles of the present invention exhibit good stability of activity on extended use. These results are highly unexpected in view of the fact that prior art teachings indicate that large-pore alumina is required to prevent rapid catalyst deactivation in hydrotreating of petroleum residuums, which normally contain metallic contaminants. Quite the contrary to such teachings, the present invention provides good stability of catalyst activity in hydrotreating such residuums and, at the same time, provides good activity throughout normal use.

The invention will be described further with reference to the accopanying drawings, in which:

Figure 1 is a graph comparing the Average Relative Volume Activities of shaped catalyst particles contemplated by the present invention with conventional catalyst particles of the prior art;

Figure 2 is a graph comparing the Average Relative Weight Activities of the same cata-

lyst particles considered in Figure 1;

Figure 3 is a graph comparing the Relative Activities of catalyst particles of the present invention with those of catalyst particles of the same composition having conventional configuration, the comparisons being under prescribed conditions;

Figure 4 is a graph comparing the Average Relative Weight Activities of catalyst particles of the present invention with conventional catalyst particles of like composition;

Figure 5 and 5A illustrate a "plate", a convex catalyst not contemplated by this invention, wherein the dimensions are L=0.186 inch. D=0.094 inch, and d=0.056 inch;

Figures 6 and 6A illustrate a "dumbbell" configuration of this invention wherein the dimensions are L=0.202 inch, D=0.0473 inch, and d=0.0532 inch;

Figures 7 and 7A illustrate a "figure eight" configuration of this invention wherein the dimensions are L=0.1814 inch, D=0.092 inch, and d=0.0541 inch;

Figures 8 and 8A illustrate "three-leaf clover" trilobal configuration of this invention wherein the dimensions are L=0.212 inch, D=0.0919 inch, d=0.0477 inch, T=0.0442 inch, and α=60°;

Figure 9 illustrates an undimensioned oval convex configuration not contemplated by this invention;

Figure 10 illustrates an undimensioned tetralobal configuration of this invention;

Figure 11 illustrates an undimensioned ring or "donut" configuration contemplated by this invention;

Figure 12 represents mercury penetration of catalyst particles in pore volume and the pore size distribution analysis, the larger curves showing pore size and the smaller curves showing the relationship of pore size to total pore volume; and

Figure 13 is a graph of sulfur removal against time of service use for catalysts of the present invention and a comparative catalyst in hydrotreating of petroleum residuum.

The invention is illustrated by the examples which follow wherein all parts and percentages are by weight unless otherwise specifically illustrated.

The examples are divided into groups distinguished by either a letter or number designation. The lettered examples illustrate use of catalyst particles of this invention in hydrotreating processes involving fuel oils while the numbered examples illustrate use of catalyst particles of this invention in hydrotreating processes involving petroleum residuums. In both groups of examples, advantages in activity as a result of catalyst shape are shown. In the lettered group of examples, no specific advantages with respect to pore diameter are apparent so that details as to pore diameter are not presented; the pore diameters are however within the scope of this invention In the numbered group of examples, where specific advantages result from pore diameter, these values are given. Thus, the numbered examples illustrate the combination of various characteristics of catalyst particles that constitute the product aspect of the present invention and illustrate hydrotreating of petroleum residuum using the catalyst particles of the invention, which constitutes the process aspect of the present invention.

Examples A—G.

A series of shaped particles were made as follows:

One thousand and thirty gallons of water are charged to an agitated tank. Over a period of about 45 minutes, 3,940 lbs. of sodium aluminate solution (28% Al_2O_3, about 15% excess Na_2O) and 5,430 lbs. of aluminum sulfate solution (7.8% Al_2O_3) are metered into the water heel. The rates are adjusted so as to hold the pH at about 8.5. When the aluminum sulfate solution is used up, the sodium aluminate solution flow is continued so as to bring the pH of the batch to 10.5. The batch temperature should be about 120°F. when the final pH is reached.

The resulting alumina slurry above is filtered and washed (using 9.0 pH water) over a rotary vacuum filter to remove the sulfate. Nitric acid is added to the repulped washed cake to adjust the pH down to 7.0—7.5. The pH adjusted slurry is washed over another filter to remove the Na_2O.

The resulting washed slurry above is spray dried to give a coarse powder.

The spray dried alumina powder (363 pounds) is charged to the muller along with 425 pounds of water. Thereafter 285 pounds of ammonium molybdate solution (28% MoO_3) followed by 108 pounds of cobalt nitrate solution (16% CoO) are added to the mix.

The batch is mixed for a period of about 10—15 minutes, then 75 pounds (ignited basis) of alumina powder is added to the mix, after which the batch is mulled for an additional 10—15 minutes.

Using the desired die (shape of extrudate) the muller mix is extruded through an extruder (Welding Engineer Extruder 2010). The extrudates are cut, dried in an oven to about 20% loss on ignition, and then calcined at a temperature of 1200° F. for 1 hour.

The above procedure is a procedure used to produce Examples H, I, J and K referred to below. Examples A, B, C, D, E, F and G and L and M are prepared in essentially the same manner except that the cobalt nitrate solution and ammonium molybdate solution usage would be adjusted to give a 6% CoO—12% MoO_3 content as opposed to 3% cobalt oxide — 15% molybdenum oxide content of Examples H—K. In this series normal

"1/16" and "1/18" inch extrudates (cylinders) were made for reference purposes. These catalysts and catalysts of this invention are compared employing the following described Gas Oil Test for desulfurization and denitrogenation.

Gas Oil Test
Gas Oil Description
Gravity=23.3° API
Boiling Range=490—847° F.
Sulfur Content=1.0%
Basic Nitrogen Content=515 ppm

The catalyst is charged into the reactor by volume. Two 25 cc. catalyst beds are used in series. Each of these beds is diluted with glass beads to a total of 100 cc's. The beds are separated with a glass wool plug.

The catalyst is then presulfided as follows:

1. The reactor is heated to 600° F. in flowing nitrogen at atmospheric pressure.

2. At 600° F. the nitrogen is stopped and a mixture of 90% H_2 plus 10% H_2S by volume is passed over the catalyst at 0.85 SCF/hr. for 30 minutes.

3. The reactor temperature is then raised to 700° F. and held for 2 hours with the H_2/H_2S mixture as in 2.

4. After 2 hours the reactor temperature is reduced to 450° F. with H_2/H_2S flowing. This completes the presulfiding.

The process conditions used are as follows:

Temperature=650 and 725° F.
Pressure=750 psig
Space Velocity=2 LHSV
Hydrogen Recycle Rate=1000 SCF/Bbl

Three samples are collected at each temperature. These samples are scrubbed with nitrogen and a portion is then analyzed for basic nitrogen by U.O.P. method 269—59. The remaining portion of the sample is washed with distilled water three times when analyzed for sulfur by the Dohrmann sulfur analysis. Since this is a diffusion influenced reaction the size of the particle affects its activity. Results for these two cylinders (1/8 inch and 1/16 inch extrudates) are used to establish the diffusion curve. Activities obtained for shaped particles are then compared to the diffusion curve at equal particle size. In order that different shaped particles can be readily compared, particle size is defined in terms of its volume to external surface ratio, V_p/S_p.

In this study two (2) shapes other than cylinders were made. One of these has been designated the "dumbbell". The other has been termed a "3 leaf clover". The particular "dumbbell" is illustrated in Figure 6 of the accompanying drawings and the particular "3 leaf clover" is illustrated in Figure 8.

In Table I set forth below activity results for these catalysts are shown. Equal volumes of the catalyst are charged and both sulfur and nitrogen removals are measured at two temperatures as described above. Recent calculations have shown that at both 650° F. and 725° F. the reactor operates in the "trickle" phase (hydrocarbon exists as both liquid and vapor). In Series I (Catalyst A—D) the catalysts were *muffle calcined* in a common batch. The series II catalyst (Catalyst E—G) were *rotary calcined* in separate batches. Activity results are displayed in terms of percentage removals and relative activities on both a weight and volume basis. The relative activities are the most meaningful numbers. They are simply defined as the ratio of second order rate constants (catalyst activity) for the catalyst of interest to that of the reference catalyst. In each series the 1/16 inch cylinder was defined to be 100 activity. Relative activities can be simply interpreted as the percentage of activity of the reference catalyst (1/16 inch cylinder).

In Series I both the relative weight and volume sulfur activities of the shaped particles are greater than that of the 1/16 inch cylinder. In Series II, with the exception of one data point which is not believed to be statistically significant, a similar advantage for sulfur removal is evident. Although the two series do not agree exactly (possibly due to differences in calcination) their average results shown that the shaped particles have more sulfur removal activity on both a weight and volume basis.

In Table II, set forth below, the physical properties of the catalysts are given. The significant dimension in terms of *generalized particle size* is the V_p/S_p ratio. This ratio shows that the order of increasing size is:

1/16" Cyl.<dumbbell<3 leaf clover< 1/8" Cyl. With respect to *diffusion* the relative activities should increase with decreasing V_p/S_p. The Gas Oil Test results, however, do not correalate with V_p/S_p. Rather, they show an unexpected advantage for the shaped particles. If another mode of mass transfer is affecting the results, bulk mass transfer, then one might expect that the Gas Oil Test results should correlate with total geometric surface (total surface in Table II). However the activity results do not correlate with total surface and again show an unexpected advantage for shaped particles. The ABD values show that the dumbbells pack much more loosely than the other particles.

In Figure 1 of the accompanying drawings the average relative volume activities are plotted vs. particle size. The straight line shown is the diffusion curve obtained from the cylinders. It agrees well with theory. Both the dumbbell and the 3 leaf clover are above this curve which is a surprising result. The dumbbell is not as active as the 3 leaf clover

on this volume basis at least in part because of its low ABD.

A similar graph for weight activities is shown in Figure 2. Both shapes are significantly above the diffusion curve and have approximately the same activity.

Finally in Table III pressure drop data are shown for the shaped particles compared to the 1/16 inch cylinder. Both absolute pressure drops and relative pressure drops as a function of flow rate are given. In this test 50 cc. of catalyst is loaded into a tube and the pressure drop from flowing air is measured. Both shaped particles of this invention show about the same pressure drops and a significant pressure drop advantage (about 40% lower at the more important flow condition) compared to the 1/16 inch cylinder. For the dumbbell the lower pressure drop is a direct result of its low ABD. For the 3 leaf clover the lower pressure drop is a result of its increased size (V_p/S_p) and slightly lower ABD.

TABLE I.

GAS OIL TEST ACTIVITY RESULTS

Catalyst		% Removals				Relative Activities							
						Volume Basis				Weight Basis			
	Description	Sulfur		Nitrogen		Sulfur		Nitrogen		Sulfur		Nitrogen	
SERIES I		650F	725F	650F	725F	650F	725F	650F	725F	650F	725F	650F	725F
A	"1/16" Cylinder	85.6	97.5	0	30.6	100	100	—	100	100	100	—	100
B	Dumbbell	86.8	98.1	0	25.2	111	133	—	79	130	159	—	93.
C	3 Leaf Clover	86.3	97.8	1.6	33.2	106	114	—	110	109	117	—	—
D	"1/8" Cylinder	71.6	95.2	—	—	42	51	—	—	41	49	—	—
SERIES II													
E	"1/16" Cylinder	82.2	97.6	—	—	100	100	—	—	100	100	—	—
F	Dumbbell	85.8	97.2	—	—	131	85	—	—	159	103	—	—
G	3 Leaf Clover	88.2	98.5	—	—	162	161	—	—	164	163	—	—
AVERAGE I & II													
	"1/16" Cylinder	—	—	—	—	100	100	—	—	100	100	—	—
	Dumbbell	—	—	—	—	121	109	—	—	145	131	—	—
	3 Leaf Clover	—	—	—	—	134	137	—	—	137	140	—	—
	"1/8" Cylinder	—	—	—	—	42	51	—	—	41	49	—	—

TABLE II.

PHYSICAL PROPERTIES

	Catalyst Description	Length (in)	Dia. (in)	Volume Particle Vp $(in)^3$	Surface Particle Sp $(in)^2$	Vp/ S_p (in)	Total Surface area $(in)^2$	Pore Volume (PV) cc/g	Apparent Bulk Density (ABD) g/cc	Compacted Bulk Density (CBD) g/cc	Crush Strength (CS) lbs.	CS/L lbs/in
A	"1/16" Cylinder	0.216	0.052	0.00046	0.0398	0.0117	178	0.55	0.66	0.72	21.5	172
B	Dumbbell	0.202	—	0.00096	0.0798	0.0121	124	0.56	0.57	0.60	—	—
C	3 Leaf Clover	0.212	—	0.00111	0.0782	0.0142	128	0.57	0.65	0.69	31.3	250
D	"1/8" Cylinder	0.215	0.125	0.00262	0.1084	0.0241	—	.57	.67	.73	29	232

TABLE III.

PRESSURE DROP

	A		B		C	
Nominal Air Flow SCFM	"1/16" Cylinder ΔP "H_2O	Relative ΔP, %	Dumbbell ΔP "H_2O	Relative ΔP, %	3 Leaf Clover ΔP "H_2O	Relative ΔP, %
0+	1.5	100	0.94	61	0.98	64
1	4.0	100	2.6	64	2.6	64
2	15.7	100	11.2	71	11.1	71
3	36.4	100	27.0	75	26.3	72

Examples H—J.

Additional examples for shaped catalytic particles are herein reported. A muller mix prepared as described above of a 3% cobalt oxide, 15% molybdenum oxide balance alumina was used to extrude these particles (1/16, 1/8" cylinders, dumbbell and 3 leaf clover). Activities were obtained on a Heating Oil Test described below:

Heating Oil Test
Heating Oil Description
Gravity=34.2° API
Boiling Range=435—628° F.
Sulfur Content=1.4%
Basic Nitrogen=35 ppm

The catalyst is charged to the reactor by volume. Two 25 cc. catalyst beds are used in series. Each of these beds is diluted with glass beads to a total 55 cc's. The beds are separated with a glass wool plug.

The catalyst is then presulfided via the following scheme:

1. The catalyst is heated from room temperature to 700° F. in a mixture of 10% H_2S plus 90% H_2 flowing at 5 SCF/Hr. at atmospheric pressure.

2. The catalyst is then held at 700° F. in this mixture for 1 hour.

3. The reactor temperature is then lowered under flowing hydrogen to 600° F.

The process conditions used are as follows:

Temperature=600, 700° F.
Pressure=500 psig
Space Velocity=4 LHSV
Hydrogen Recycle Rate=1000 SCF/Bbl

Three samples are collected at each temperature. These samples are scrubbed with caustic: water: caustic and finally water again. They are then sent for Dohrmann Sulfur analyses.

The activity results are shown in Table IV. The results show an advantage for shaped particles. A graphical presentation of the data is given in Figure 3 for the 700° F. point. Activities for the shaped particles are above the diffusion curve. Finally, physical properties of the catalyst compared are given in Table V.

TABLE IV

HEATING OIL RESULTS

Catalyst ID	Description	% Sulfur Removal 600°F	% Sulfur Removal 700°F	% Relative Activities Volume 600°F	% Relative Activities Volume 700°F	% Relative Activities Weight 600°F	% Relative Activities Weight 700°F
H	"1/16" inch cylinder	46.1	86.5	100	100	100	100
I	Dumbbell	43.0	87.3	88	107	106	128
J	3 Leaf Clover	49.6	88.1	115	116	115	116
K	1/8" Cylinder	44.0	85.0	92	88	87	83

TABLE V

PHYSICAL PROPERTIES

I.D.	Description	Length (in.)	Dia. (in.)	Volume particle Vp $(in.)^3$	Surface particle Sp $(in.)^2$	Vp/Sp (in.)	PV cc/g	ABD g/cc	CBD g/cc	CS lbs.	CS/L lbs./in.
H	"1/16" inch Cylinder	.142	.053	.000316	.0282	.0112	.50	.71	.76	12.3	93
I	Dumbell	.177	—	.000838	.0704	.0119	.50	.60	—	—	—
J	3 Leaf Clover	.180	—	.000933	.0695	.0134	.51	.70	.74	23.3	174
K	1/8" Cylinder	.201	.115	.00209	.0934	.0224	.51	.74	.78	27.7	223

TABLE VI

GAS OIL TEST ACTIVITY RESULTS

Catalyst I.D.	Description	% Sulfur Removal 650F	% Sulfur Removal 725F	% Relative Activities Volume 650F	Volume 725F	Weight 650F	Weight 725F	Vp/Sp in.	Concavity C
L	Figure Eight	86.2	97.8	117	112	120	115	.0139	1.04
M	Flat Plate	85.3	96.9	110	78	104	74	.0154	1.00

TABLE VII

PHYSICAL PROPERTIES

I.D.	Description	Length (in.)	Dia. (in.)	Vp $(in.)^3$	Sp $(in)^2$	Vp/Sp in.	PV cc/g	ABD g/cc	CBD g/cc	CS lbs.	CS/L lbs./in.
L	Figure Eight (Fig. 7 Drawings)	.181	—	.000756	.0544	.0139	.55	.64	.71	52	415
M	Flate Plate (Fig. 5 Drawings)	.187	—	.000874	.0567	.0154	.56	.68	.72	57	455

Examples L—M.

Using the same catalyst material as was used in Examples A—G and the same test, these catalysts were rotary calcined as were the Series II catalysts in Table I hereinbefore.

The shapes studied were a figure eight with a small amount of concavity, C=1.04, and a flat plate which is convex, C=1.00, but with a non-circular cross section. These results are shown in Table VI. The average results from catalyst A and catalyst C were used to calculate the relative activities in Table VI. To simplify the data interpretation the average relative weight activities (650° F. and 725° F.) is plotted as a function of particle size in Figure 4. In general those particles with a concavity index, C, equal to 1.00 fall on the diffusion curve. The figure eight with C=1.04 falls above the diffusion curve but not as high as those with C=1.10 or greater. These data tend to support the hypothesis that C must be greater than 1.00. Figure 4 demonstrates that. Preferably, C should be in the neighborhood of 1.10.

It will be apparent that the above-described invention and parameters relate to freshly prepared catalyst particles of unique size and shape and does not contemplate conventional catalyst shaped and size having imperfection therein of the type that may be described as knicks, chips, abrasions, bends and the like.

In Example A—M, inclusive, the advantages in activity in processing gas oils is apparent for catalysts of unique shape. In hydrotreating gas oils, however, a wide range of average pore diameter in the catalyst material may be used effectively, i.e., the activity values appear to be influenced by the shape factor apart from any influence resulting from average pore diameter. This is apparently due to the fact that the gas oils have a relatively low boiling range, reflecting relatively low molecular weight of components, and are essentially free from metallic components.

In the numerical examples which follow, hydrotreating is effected on petroleum residuums, which contain metallic contaminants and have a higher boiling range than gas oils, reflecting relatively higher molecular weight components than in gas oil. These properties of the feedstock processed have been held to influence the specific average pore diameter of catalysts that can effectively be employed. Therefore, in the numerical examples the average pore diameter values are given.

Example 1.

A precipitated alumina was prepared employing silica hydrogel in the heel used to prepare the strike. The resulting precipitate was washed free of salts. Ammonium heptamolybdate $[(NH_4)_6Mo_7O_{24}]$ and water were added to form a spray-dryer feed and spray drying was carried out in accordance with conventional procedures.

To 35 pounds of the spray dried powder was added 34 pounds of water and 107 milliliters of concentrated HNO_3. The mixture was mulled to an extrudable consistency and then extruded using a die containing orifices in the "clover-leaf" shape. The extrudates were dried at 120° C. for 16 hours and then calcined at 650° C. for 1 hour.

An 800 gram portion of the calcined ex-

trudates was impregnated with an aqueous solution of 136 grams $Co(NO_3)_2 . 6H_2O$ and 53 grams urea. The impregnated extrudates were dried at 120° C. for 16 hours and then calcined at 650° C. for 1 hour.

Extrudate properties are given in Table VIII, porosity in Figure 12, and activity in Figure 13.

Example 2.

The procedure of Example 1 was followed in every material detail except that drying and calcining of the extrudate was carried out in the presence of a positive air flow by placing a vacuum line beneath the catalyst particles placed in a rack. The air flow was employed in the drying and calcining steps prior to and subsequent to impregnation.

Extrudate properties are also given in Table VIII and Figures 12 and 13.

Comparative Example 1.

A spray dried precipitated alumina was prepared according to conventional procedures. To 20 pounds of the alumina was added 5 pounds of silica hydrogel of 7.2% calcined solids, 2.84 pounds of $Co(NO_3)_2 . 6H_2O$, 2.68 pounds of

$$(NH)_6Mo_7O_{24} . XH_2O,$$

1.12 pounds urea, 14.0 pounds water, 1.5 pounds ammonia hydroxide (28% NH_3), and 80 grams of Superfloc (a high molecular weight polacrylamide). The mixture was mulled to an extrudable consistency and extruded as "clover-leaf" extrudates. The extrudates were dried at 120° C. for 16 hours and calcined at 650° C. for 1 hour.

Extrudate properties are also given in Table VIII and Figures 12 and 13.

In Table VIII, it can be seen that the major differences in catalysts of the present invention and that of the prior art (Comparative Example 1) are the total pore volume, mean pore diameter, and compacted bulk density, the latter property being influenced by total pore volume.

In Figure 12, the specific distribution of pore diameters in the catalyst materials can be seen and it can be readily appreciated that the majority of pores of catalysts of the present invention are within a narrow range of diameters in the range of 40—90 Å units as measured.

In order to evaluate the catalysts for activity over an extended time period, the following test procedure was employed.

A suitable reactor was employed which contains two fixed beds in series each of a volume of 100 milliliters. In the case of the catalysts of Example 1 and Comparative Example 1, the beds were each filled with 50 milliliters of glass beads and 50 milliliters of glass beads intimately mixed. In the case of the catalyst of Example 2, the beds were each filled with 100 milliliters of catalyst alone.

The catalysts were pretreated in a nitrogen atmosphere at 600° F. and then contacted with a gaseous mixture of 90 mole percent H_2 and 10 mole percent H_2S at 600—700° F. for 2 hours at an absolute pressure of 50 pounds per square inch.

In the hydrotreating reaction, a residuum feedstock of the following properties was employed:

Kuwait Atmos. Resid.	
Gravity API	22.4
Sulfur Weight Percent	3.6
Metal Parts Per Million	
V	45
Ni	12
Na	10
Basic N	289

Hydrogen gas and the residuum were mixed together and fed into the top of the reactor. The conditions maintained during reaction were as follows:

Temperature	725° F.	
Liquid Hourly Space Velocity	0.5	reciprocal hour
G_3 addition rate	1000	SCF/barrel oil
Total Pressure	800	pounds/inch² gauge

After various time intervals of reaction, the percent sulfur removal was determined and the data plotted as a function of time of operation. In the case of Example 1, duplicate runs were made. The results are shown in Figure 13.

From Figure 13, it can be readily seen that sulfur removal is greater for the catalyst of the present invention than for the prior art catalyst. It can also be seen that as the time of use for a catalyst increases, the prior art catalyst shows a much greater loss in activity than does the catalyst of the present invention.

TABLE VIII.

SHAPED EXTRUDATE PROPERTIES

Property	Example 1	Example 2	Comparative Example I
Pore Volume (H_2O) ml.	0.49	0.47	0.76
Pore Volume (Hg)* ml.	0.45	0.41	0.75
Surface Area (N_2) m^2/gm	237	—	211
Surface Area (Hg)* m^2/gm	243	254	195
Mean Pore Diameter (Hg)* Å	68	54	146
Compacted Bulk Density g./l	.76	.80	.55
Particle Length (inch)	0.114	0.135	0.12
Maximum Diameter (D) (inch)	0.51	0.51	0.53
Composition Weight Percent			
CoO	4	4	4
MoO_3	12	12	12
SiO_2	2	2	2
Al_2O_3	Balance	Balance	Balance

*140° Contact Angle

WHAT WE CLAIM IS:—

1. A porous hydrotreating catalyst particle having a composition comprising a major portion by weight of alumina, optionally up to 36 weight percent of silica, based on the total weight of silica and alumina; from 10 to 20 weight percent of molybdenum oxide and a total of 1 to 8 weight percent of an oxide selected from cobalt and nickel oxides and mixtures thereof, said percentages being based on the total weight of said catalyst particle; said particle being in the form of a concave geometric solid; said solid being characterized by a concavity index greater than 1.0, a void fraction in the range of 0.25 to 0.60, a particle size defined by a ratio of geometric volume to geometric surface in the range of 0.001 to 0.042 inch, a catalytic surface area greater than 150 square meters per gram, and a catalytic pore volume in the range of 0.35 to 0.85 cubic centimeters per gram; said pore volume resulting from a major portion of pores of diameter in the range of 40 to 90 Angstrom units when measured with mercury at up to 50,000 pounds per square inch absolute pressure and a contact angle of 140°.

2. A catalyst particle according to Claim 1, wherein the concavity index is from 1.05 to 1.15.

3. A catalyst particle according to Claim 1 or Claim 2, wherein the void fraction is in the range of 0.35 to 0.50.

4. A catalyst particle according to any preceding Claim, wherein the ratio of geometric volume to geometric surface is in the range of 0.005 to 0.025 inch.

5. A catalyst particle according to any preceding Claim, wherein the catalytic surface area is greater than 200 square meters per gram.

6. A catalyst particle according to any preceding Claim, wherein there is present up to 5 weight percent of silica as SiO_2, based on the total weight of silica and alumina.

7. A catalyst particle according to any preceding Claim, wherein there is present up to 45 weight percent of a zeolite based on the total weight of zeolite and alumina.

8. A catalyst particle according to any preceding Claim, wherein molybdenum oxide is present in the amount of 12 weight percent and cobalt oxide in the amount of 4 weight percent.

9. A catalyst particle according to any preceding Claim, said particle being further characterized by a trilobal cross-sectional shape defining said concave geometric-solid; said trilobal cross-sectional shape being such that the lobes are defined by circles having equal diameters, the centers of which circles are spaced from each other so that lines joining

said centers form an equilateral triangle.

10. A catalyst particle according to any preceding Claim which has been sulfided.

11. A process for hydrotreating a petroleum residuum, which process comprises contacting said residuum with a fixed bed of catalyst particles according to any preceding Claim, in the presence of hydrogen at a flow rate of 500 to 5,000 standard cubic feet per barrel of oil at a liquid hourly space velocity of 0.20 to 5.0 reciprocal hour, at a temperature in the range of 600° to 850° F., and at a total pressure in the range of 200 to 10,000 pounds per square inch gauge.

12. A process according to Claim 11 wherein the hydrogen flow rate is 2,000 to 4,000 standard cubic feet per barrel of residuum.

13. A process according to Claim 11 or Claim 12, wherein the liquid hourly space velocity is 0.2—0.8 reciprocal hour.

14. A process according to any one of Claims 11—13, wherein the temperature is 650°—750° F.

15. A process according to any one of Claims 11—14, wherein the total pressure is 600—1000 pounds per square inch gauge.

16. A process according to Claim 11, wherein the hydrogen flow rate is 1,000 standard cubic feet per barrel of oil, the liquid hourly space velocity is 0.5 reciprocal hour, the temperature is 725°., and the total pressure is 800 pounds per square inch gauge.

17. A process for hydrotreating a petroleum residuum, according to Claim 11 and substantially as hereinbefore described.

18. A petroleum product obtained by a hydrotreating process according to any one of Claims 11 to 17.

19. A porous hydrotreating catalyst particle, according to Claim 1 and substantially as described in any one of the Examples herein.

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1 446 175 COMPLETE SPECIFICATION
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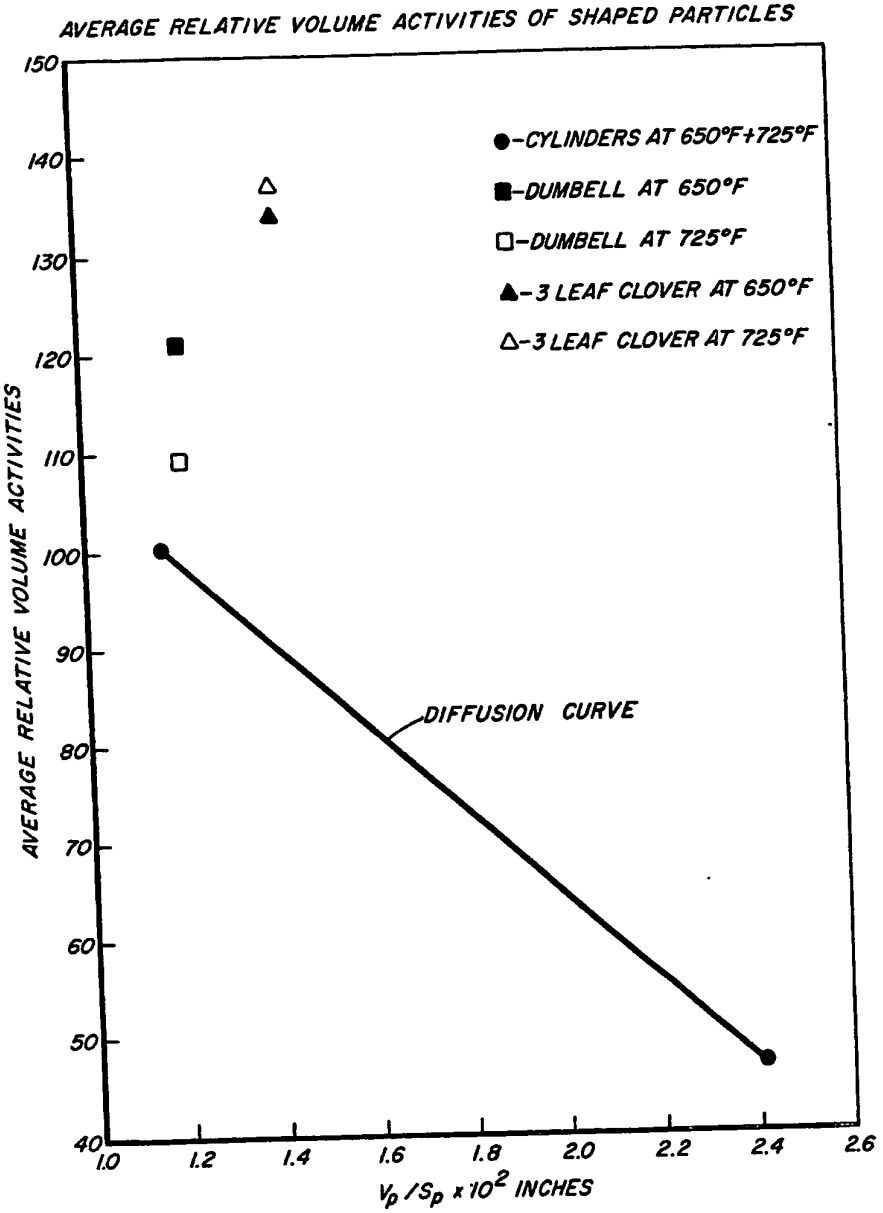

FIG. 1

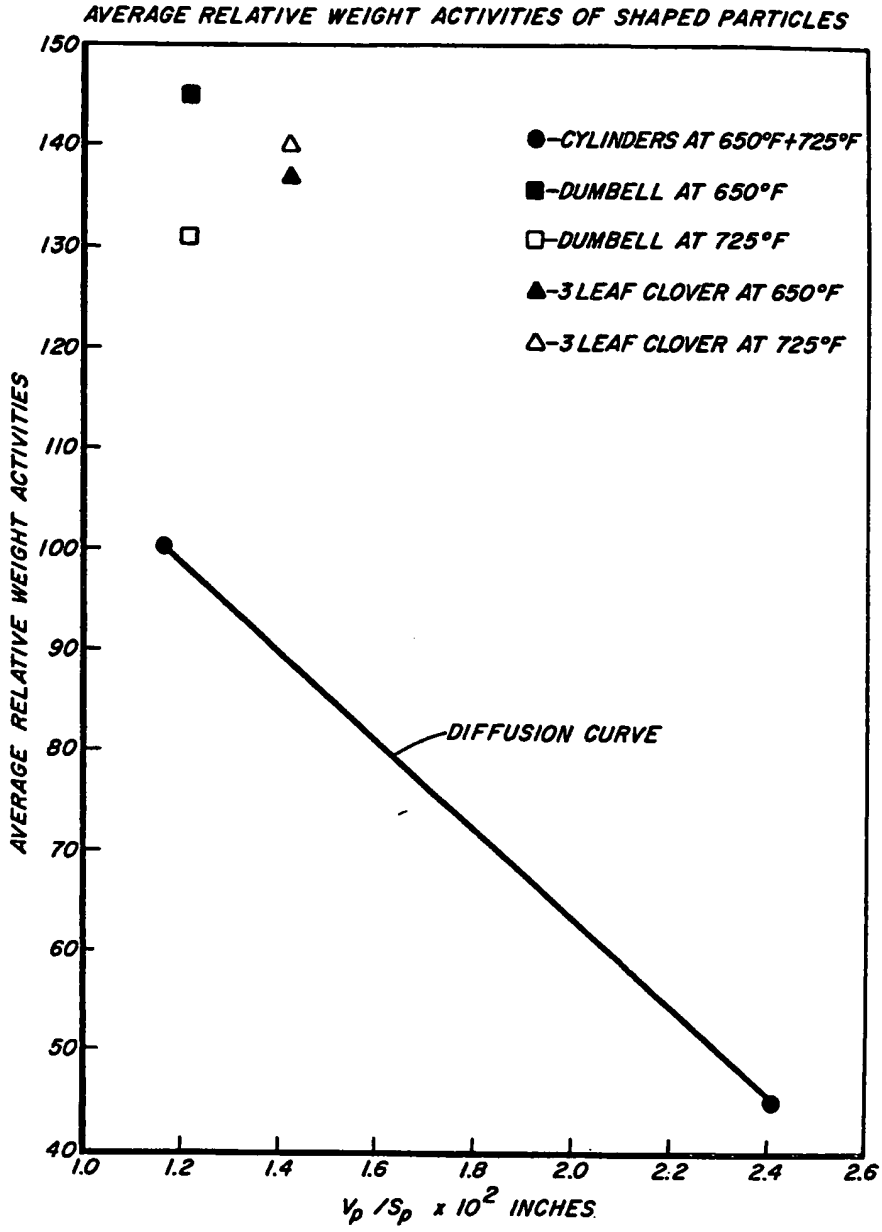
AVERAGE RELATIVE WEIGHT ACTIVITIES OF SHAPED PARTICLES
AVERAGE RELATIVE WEIGHT ACTIVITIES
150
140
130
120
110
100
90
80
70
60
50
40
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
Vp /Sp x 10² INCHES
●–CYLINDERS AT 650°F+725°F
■–DUMBELL AT 650°F
□–DUMBELL AT 725°F
▲–3 LEAF CLOVER AT 650°F
△–3 LEAF CLOVER AT 725°F
DIFFUSION CURVE

FIG. 2

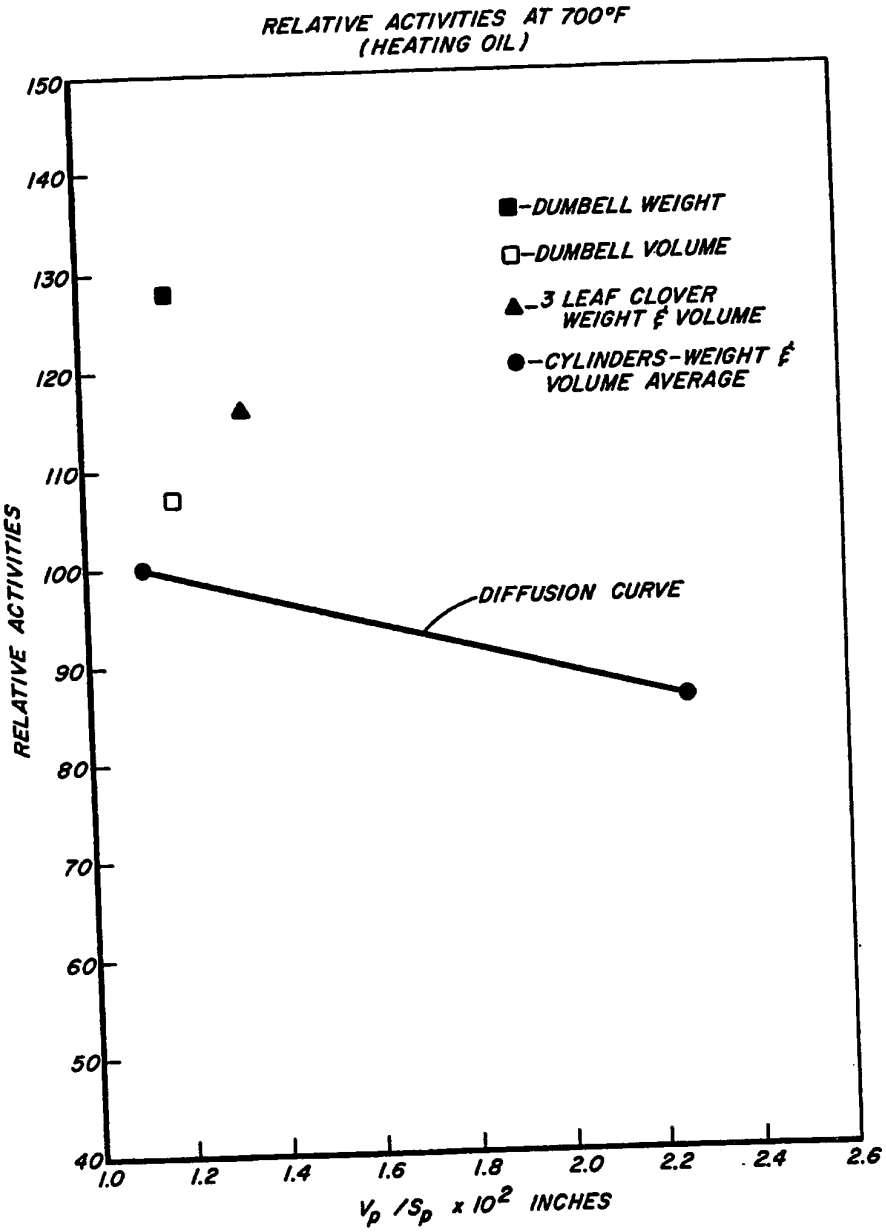
RELATIVE ACTIVITIES AT 700°F
(HEATING OIL)
150
140
130
120
110
100
90
80
70
60
50
40
RELATIVE ACTIVITIES
■-DUMBELL WEIGHT
□-DUMBELL VOLUME
▲-3 LEAF CLOVER WEIGHT & VOLUME
●-CYLINDERS-WEIGHT & VOLUME AVERAGE
DIFFUSION CURVE
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
$V_p / S_p \times 10^2$ INCHES

FIG. 3

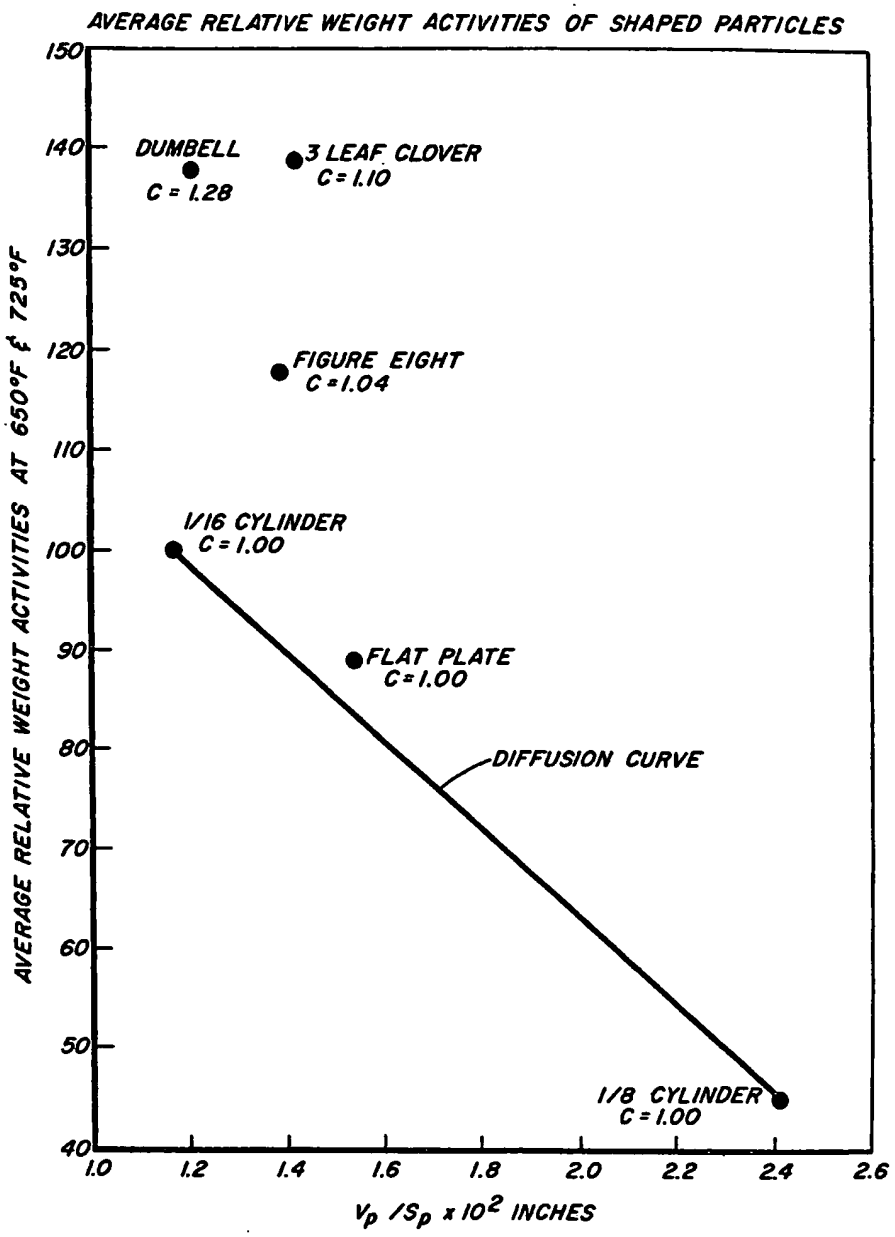
AVERAGE RELATIVE WEIGHT ACTIVITIES OF SHAPED PARTICLES
AVERAGE RELATIVE WEIGHT ACTIVITIES AT 650°F & 725°F
150
140
130
120
110
100
90
80
70
60
50
40
DUMBELL
C = 1.28
3 LEAF CLOVER
C = 1.10
FIGURE EIGHT
C = 1.04
1/16 CYLINDER
C = 1.00
FLAT PLATE
C = 1.00
DIFFUSION CURVE
1/8 CYLINDER
C = 1.00
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
$V_p / S_p \times 10^2$ INCHES

FIG. 4

1 446 175 COMPLETE SPECIFICATION
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SHEET 5

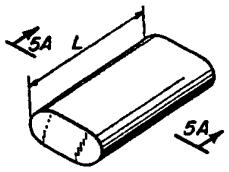

FIG.5

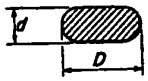

FIG.5A

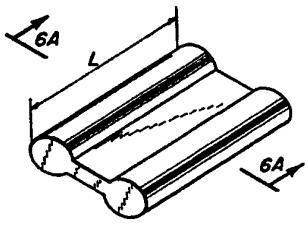

FIG.6

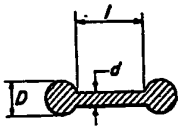

FIG.6A

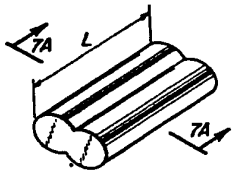

FIG.7

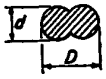

FIG.7A

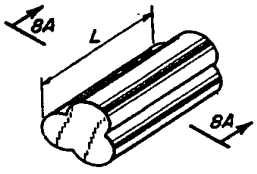

FIG.8

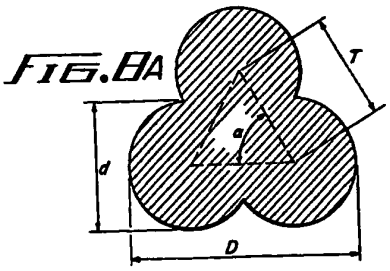

FIG.8A

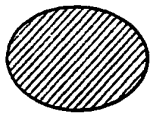

FIG.9

FIG.10

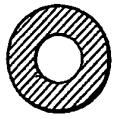

FIG.11

1 446 175
7 SHEETS

COMPLETE SPECIFICATION

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SHEET 6

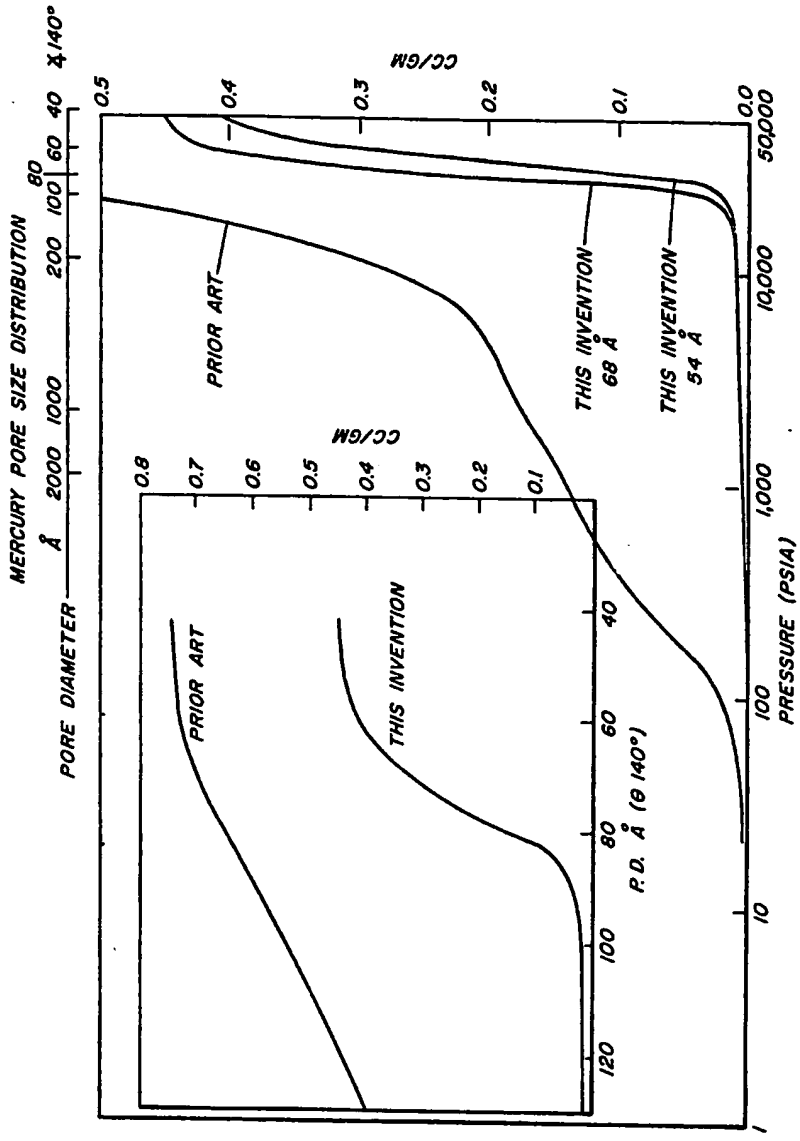

FIG. 12

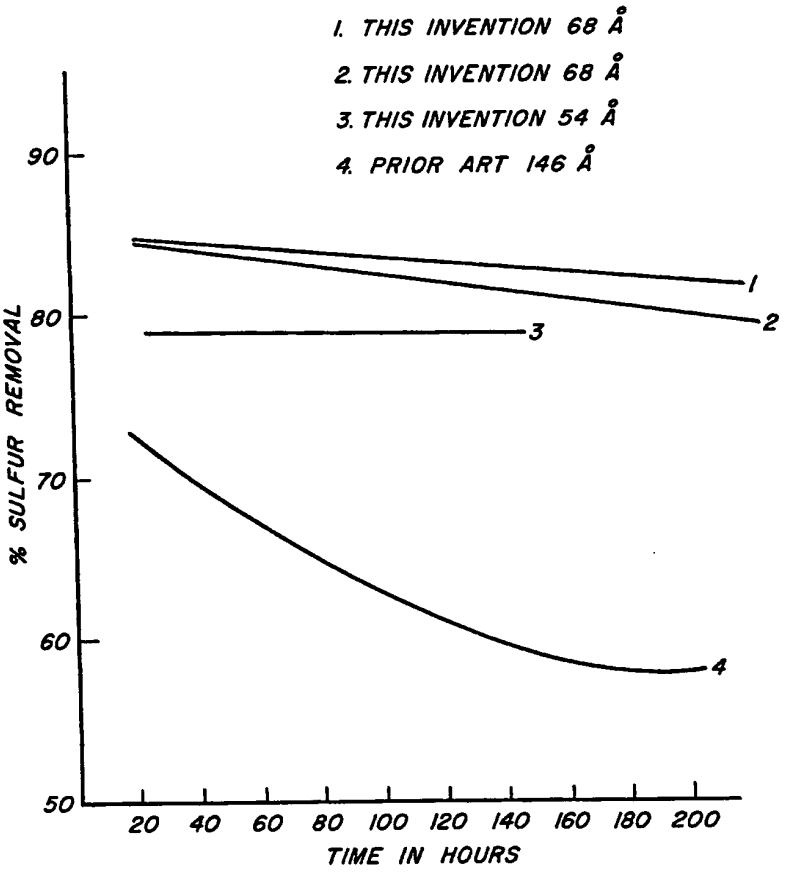
1. THIS INVENTION 68 Å
2. THIS INVENTION 68 Å
3. THIS INVENTION 54 Å
4. PRIOR ART 146 Å
% SULFUR REMOVAL
90
80
70
60
50
20 40 60 80 100 120 140 160 180 200
TIME IN HOURS
1
2
3
4

FIG. 13